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A STUDY OF NON-LINEAR ADSORPTION BY MEANS OF GAS CHROMATOGRAPHY

RALPH J. REEDER

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THESIS

A STUDY OF NON-LINEAR ADSORPTION
BY MEANS OF
GAS CHROMATOGRAPHY

by

RALPH J. REEDER

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Ralph J. Reeder

A STUDY OF NON-LINEAR ADSORPTION
BY MEANS OF
GAS CHROMATOGRAPHY

by

Ralph J. Reeder
//
Lieutenant, United States Navy

Submitted in partial fulfillment of
the requirements for the degree of

MASTER OF SCIENCE
IN
CHEMISTRY

United States Naval Postgraduate School
Monterey, California

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This work is accepted as fulfilling

the thesis requirements for the degree of

MASTER OF SCIENCE

IN

CHEMISTRY

from the

United States Naval Postgraduate School

ABSTRACT

A knowledge of the parameters of adsorption theory is valuable in the study of surface phenomena. Apparatus, procedure, and calculations are described for the determination of these parameters in the case of the adsorption of carbon dioxide on charcoal. A theory of elution adsorption chromatography is discussed and a differential equation developed to describe the eluent concentration profile of carbon dioxide from a charcoal adsorption column. The results of numerical analyses of chromatographs are given.

The writer wishes to express his appreciation for the assistance and encouragement given him by Professor John Schultz of the United States Naval Postgraduate School in this investigation.

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TABLE OF SYMBOLS

a	Constant = $1/P_r^{\circ} \nu_u k$
a_o	Constant = $\ln_e A$ for a particular run.
a_1	Constant = α for a particular run.
A	Function of adsorbate charge.
b	Constant = $a + 1/\nu_u$
B	Function of column length.
B'	Function of ordinal number of vessel.
c	Concentration in mobile phase in moles/liter.
G	Subscript; refers to gas phase.
j	Number of vessels.
k	Constant; characteristic of adsorbant-adsorbate pair.
M_s	Mass of adsorbant in each vessel in grams.
n	Constant.
p	Partial pressure of adsorbate in centimeters of mercury.
p_r	Partial pressure of adsorbate in vessel r in atmospheres.
P_r°	Total pressure in vessel r in atmospheres.
r	Ordinal number of vessel = $1, 2, 3, \ldots j$.
s	Subscript; refers to solid or adsorbed phase.
S	Displacement of curve from base line in arbitrary units.
t	Time in minutes measured from t_o.
t'	Relative time in minutes = $t - \beta - t_1$.
t_1	Time of front breakthrough.
t_o	Time of sample injection.

TABLE OF SYMBOLS (Cont'd)

v	Volume (at STP)* of gas adsorbed per unit mass of adsorbant in milliliters.
v_u	Volume (at STP)* of gas adsorbed per unit mass of adsorbant when unimolecular layer is complete.
V	Volume of mobile phase passed through column or vessel in milliliters measured from time t_o.
V_G	Volume of inert mobile phase in each vessel in milliliters.
V	Flow rate in milliliters/minute (average over the front).
$X_{G,r}$	Concentration of adsorbate in gas phase in vessel r in milliliters per milliliter.
$X_{S,r}$	Concentration of adsorbate on adsorbant in vessel r in milliliters/gram.
y	Defined parameter = $\ln_e S$.
* S.T.P.	Standard Temperature and Pressure (for this project taken as 70°C and 760 mm Hg pressure).
α	Parameter dependent on adsorbent adsorbate pair and sample size.
α'	Parameter dependent on adsorbent adsorbate pair and sample size.
β	Parameter dependent on adsorbent adsorbate pair and sample size.
β'	Parameter dependent on adsorbent adsorbate pair and sample size.

1. Introduction.

It was the object of this project to study the adsorption of a substance having a non-linear adsorption isotherm and to determine the feasibility of rapidly and accurately predicting the adsorption equation parameters from an elution chromatograph. To this end, it was decided to approach the problem from two sides:

a. Obtain an adsorption isotherm by classical methods, determining the adsorption equation, and calculating its parameters.

b. Obtain an elution adsorption chromatograph and by suitable mathematical techniques transform the data to the predicted isotherm.

The chromatographic methods are based on the repeated equilibrations of a component of a sample between a mobile phase and a static solid adsorbent surface. This method then may be used to give information about the equilibria involved; in particular with reference to the determination of the parameters of a Langmuir adsorption isotherm.

The substances chosen specifically to be studied were activated charcoal for the adsorbent and carbon dioxide gas as the adsorbate. Both substances were readily available in the required quantities and would yield the desired non-linear type of isotherm without excessive difficulty.

This report is divided by the author into sections, the order of which seem to him, to be in the most logical sequence for a complete understanding by the reader of the entire project.

2. Adsorption Theory.

Since adsorption theory is dealt with extensively in the literature, only a brief description pertinent to the current project is given here. For a more extensive treatment of the theory the reader is referred to the literature (Refs. 2,13).

At very low concentrations of solute gas in a gas adsorbant system the solute gas will distribute itself between the adsorbant and the adjacent gas phase in accordance with, what is known for liquid solutions as, Henry's Law (Ref. 13).

$$p = kv \tag{1}$$

In general, however, in adsorption this simple relation falls down for any but the lowest concentrations.

For limited ranges of concentration, an empirical equation was adopted by Freundlich (Ref. 3). This simple parabolic equation, now known as Freundlich's adsorption isotherm, has found extensive application in a great variety of cases. It can be stated in two equivalent forms:

$$v = kp^n \tag{2}$$

$$\log v = \log k + n \log p \tag{3}$$

If this relation is applicable, a plot of log p versus log v should be linear. The constant k in this case is the value of the adsorption with unit partial pressure. The constant n may have values from unity, corresponding to equation (1), at low partial pressures to some small fraction. The constant n generally decreases with increasing pressure or decreasing temperature. The limited applicability of this equation for partial

pressure ranges other than that used to determine the constants of the equation is evident when one considers that the decrease in n indicates approaching surface saturation, a condition inconsistent with the equation.

An equation proposed by Langmuir (Ref. 2) on the basis of theoretical considerations has the advantage of reducing to equation (1) at low concentrations and yielding saturation values at high concentrations. The equation

$$p = \frac{v/kv_u}{1 - v/v_u} \tag{4}$$

is a rectangular parabola passing through the origin.

The equivalent form

$$p/v = p/v_u + 1/kv_u \tag{5}$$

yields a linear plot (if the equation is applicable) when p/v is plotted versus p. The intercept on the p/v axis gives the coefficient of equation (1) at the lowest concentrations and the intercept on the p axis gives the maximum adsorption. Langmuir arrived at his relation by considering a dynamic equilibrium to exist between adsorbed and free molecules. Langmuir postulated that the adsorbate molecules distribute themselves over the adsorbant surface in an unimolecular film. Thus, evaluation of the constant v_u permits one to calculate the effective surface area of the adsorbant with the assumption that each molecule of adsorbate occupies the volume it would occupy were the unimolecular film density the same as that of the liquid adsorbate at the same temperature. More

complicated, semi-empirical extensions of the Langmuir equation postulating multimolecular films are available in the literature (Refs. 1, 5).

3. Adsorption Apparatus.

Apparatus used is shown schematically in Figure 1. The manifold (M) consisted of five hand-ground gas stopcocks lubricated with Dow-Corning High Vacuum Silicone Grease. The manometer (K), mercury filled gas burette (H), leveling bulb (G), and adsorbant vial (J) were standard laboratory ware. However, care was used in selecting the adsorbant vial so as to ensure a good vacuum fit. All joints were painted with "Glyptal" (General Electric Co. #1201 Red Enamel) to ensure their being gas tight. The vacuum pump used was a Cenco Hyvac, two stage rotary fore pump rated at ten liters per minute. The pump was connected to the manifold at stopcock (A). Stopcock (E) also acted as a relief valve when not connected to the carbon dioxide supply. The thermostat consisted of a water bath. Heat was supplied by means of electrical heating coils. Control was accomplished by using a mercury-to-mercury adjustable thermoregulator with an electronic relay. Both instruments were manufactured by the Precision Scientific Corporation and, as operated together, have a sensitivity of 0.01 degrees. A standard laboratory mixer provided circulation of the bath liquid.

The apparatus was cleaned thoroughly initially and the adsorbant vial was cleaned prior to each replacement of the adsorbant. Outgassing followed each introduction of adsorbant to the vial in order to remove traces of solvent vapor and out-gas the adsorbant prior to the run. When not in use the apparatus was closed to the atmosphere. Polyethylene flexible laboratory tubing was used where indicated. The system was

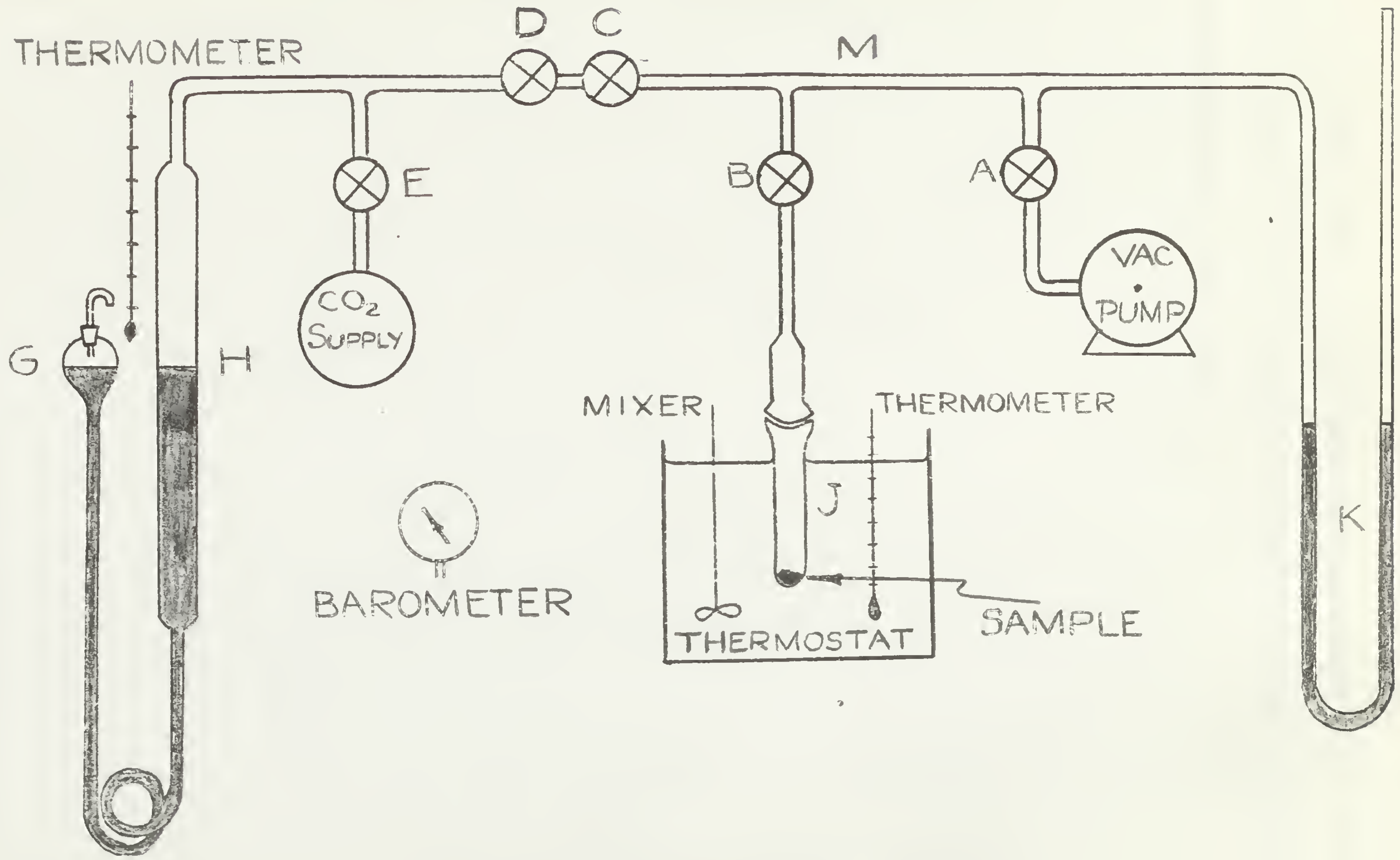


Figure 1. Adsorption Apparatus

tested for leaks under vacuum using a Tessler discharge coil. The basic apparatus and associated procedure is generally similar to that described by Daniels, et al, (Ref. 4).

4. Adsorption Procedure and Calculations.

The flexible tube connected at (E) from the carbon dioxide supply tank is flushed out by removing the vial (J) and opening stopcocks (B), (C), (D), and (E). The thermostat is brought up to temperature. Stopcock (E) is closed and the vial (J) replaced. After lowering the mercury leveling bulb as far as possible the entire system is evacuated through stopcock (A) for five minutes. Stopcock (A) is closed and the manometer reading noted. If no detectable change in the mercury level is evident over a period of ten minutes, the apparatus is assumed to be vacuum tight. Stopcock (D) is then closed and carbon dioxide admitted through (E) until the gas burette (H) is filled at atmospheric pressure. Stopcock (E) is closed and the volume of gas in the burette recorded after carefully leveling the mercury. The dead volume of the apparatus (that between the manometer and the burette) is then determined by measuring volumes of gas from the burette required to produce specified pressures with the adsorbant vial empty. This is done by introducing sufficient carbon dioxide through stopcocks (C) and (D) to produce a pressure of about 5 cm on the manometer. Ambient barometric pressure, room temperature, barometer reading and burette reading are recorded. The process is repeated at pressure increments of about ten centimeters up to atmospheric pressure. The burette is refilled when required through stopcock (E) and with stopcock (D) closed. One is now ready to commence the run. A sample of about 0.1g of charcoal (same lot as that used to make the chromato graphic column later described: High Activity Charcoal, Burrell Corp.,

Catalog No. 341-10, B.S.S. 30-80) is inserted in the adsorbant vial and with stopcock (D) closed the system is outgassed for 30 minutes. Stopcock (A) is closed. The burette is refilled and after zero readings are taken sufficient carbon dioxide is admitted from the burette to raise the pressure to about 5 cm. Small amounts of carbon dioxide are then admitted to the manometer side by alternately opening and closing stopcocks (C) and (D). The small volume of gas between the stopcocks (about 0.1 ml) is thus admitted each time in an attempt to hold the pressure constant. Alternately, one could wait for the pressure to steady for a fixed amount of carbon dioxide introduced, but this would take much longer. When equilibrium is established and the pressure is constant, readings of burette, manometer, barometer and room temperature are recorded. The addition of carbon dioxide is repeated in pressure increments of about 5 cm up to atmospheric pressure.

The volume of carbon dioxide adsorbed at equilibrium at any given pressure was obtained by subtracting the dead volume at that pressure from the total volume of gas introduced from the burette. The observed volumes, of course, were at the same conditions. For the purpose of this project all observed volumes were corrected to one atmosphere pressure (760 mm Hg) and 70° C. The corrected dead volume was determined by plotting dead volume versus pressure. The corrected adsorbed volume per unit mass of charcoal was then obtained by dividing the corrected adsorbed volume at each pressure by the weight of adsorbant used in the run.

5. Adsorption Results and Discussion.

Results of adsorption measurements are shown in Figures 2, 3, and 4. Figure 2 shows a plot of volumes of carbon dioxide adsorbed (at 80°C and one atmosphere) per gram of charcoal versus the pressure of the carbon dioxide. It is noted that the system obeys Equation (1) only over a very limited range at very low pressures. Evaluation of the slope of this plot over the range zero to ten centimeters of mercury yielded a value of 0.833 for the proportionality constant of equation (1) when pressures are expressed in centimeters of Hg and volumes in milliliters of carbon dioxide per gram of charcoal.

Figure 3 is a plot of the Freundlich isotherm, equation (2), for the resultant data at 80° C and one atmosphere. Evaluation of the slope and intercept over the lower pressure range yielded a value of 0.941 for the exponent, n, and a value of 1.24 for the coefficient, k, with quantities expressed in the same units as above. This agrees relatively well with the values of $n = 0.53$ by Taylor (Ref. 13) for the adsorption of carbon dioxide on an unmentioned grade of charcoal at 0° C. It is noted from Figure 3 that at higher pressures the value of the exponent decreases in accordance with the prediction of approaching surface saturation.

Figure 4 is a linear plot of the pressure-volume ratio versus pressure in accordance with the Langmuir isotherm, equation (5). Units and conditions are the same as for Figures 2 and 3, discussed above. It is noted that the data seem to fit this curve best and the remaining work in this project was done on the assumption of the applicability of the Langmuir

Figure 2. Pressure vs. Volume

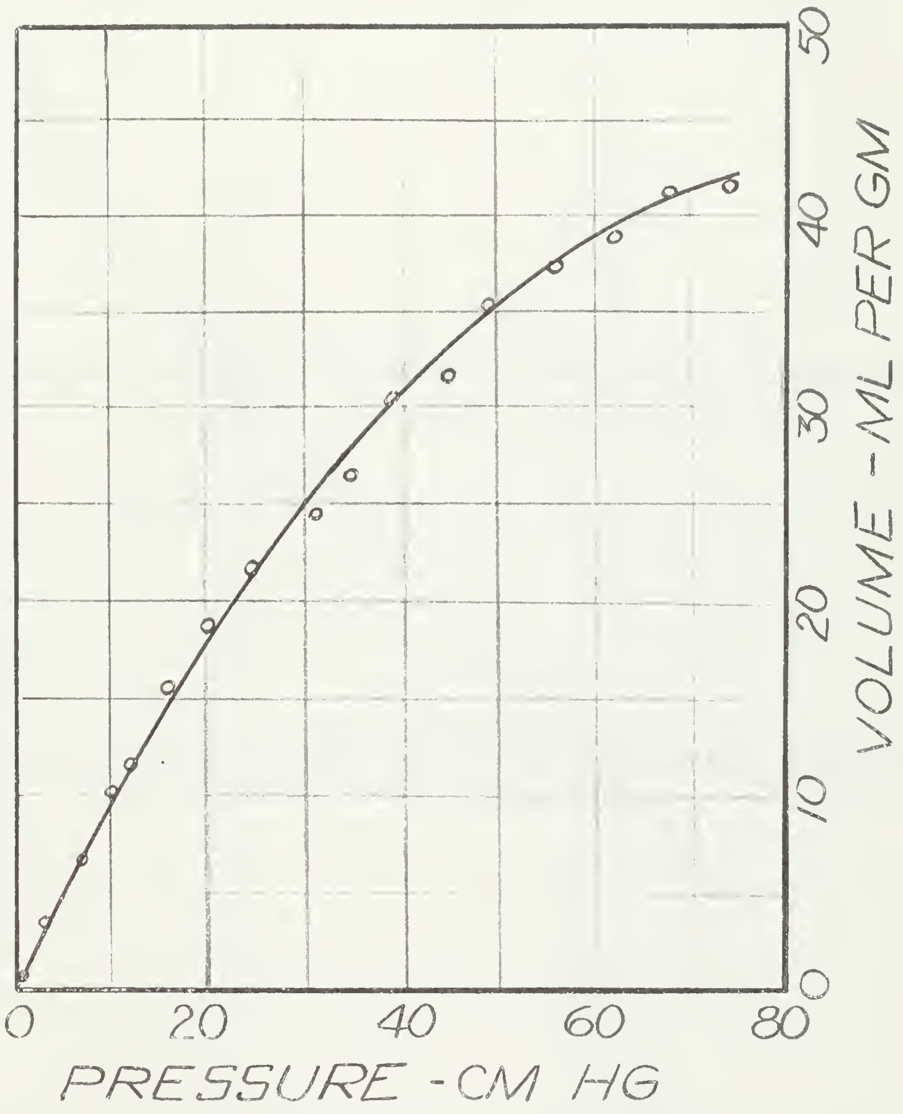


Figure 3. Freundlich Isotherm Plot

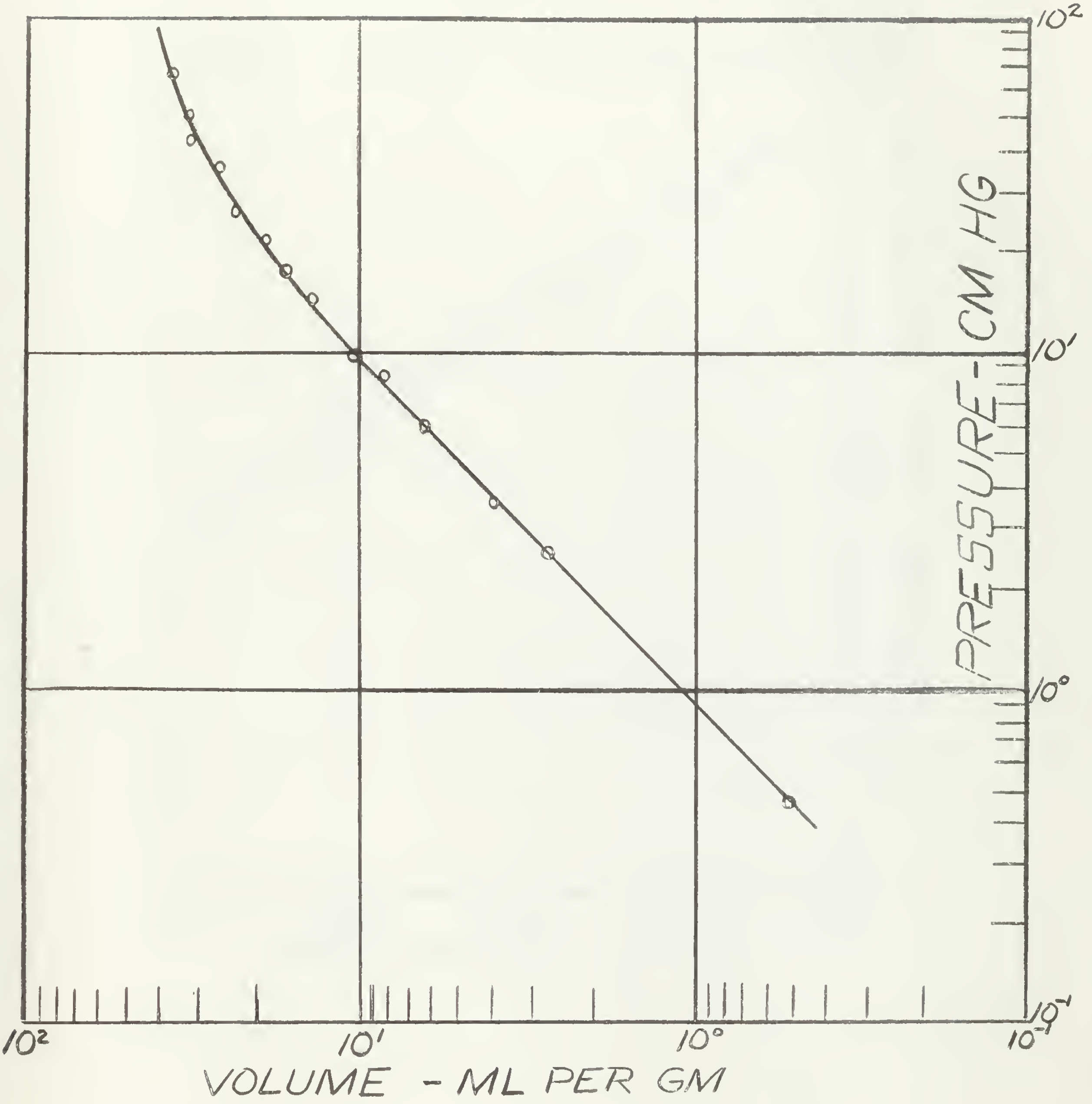
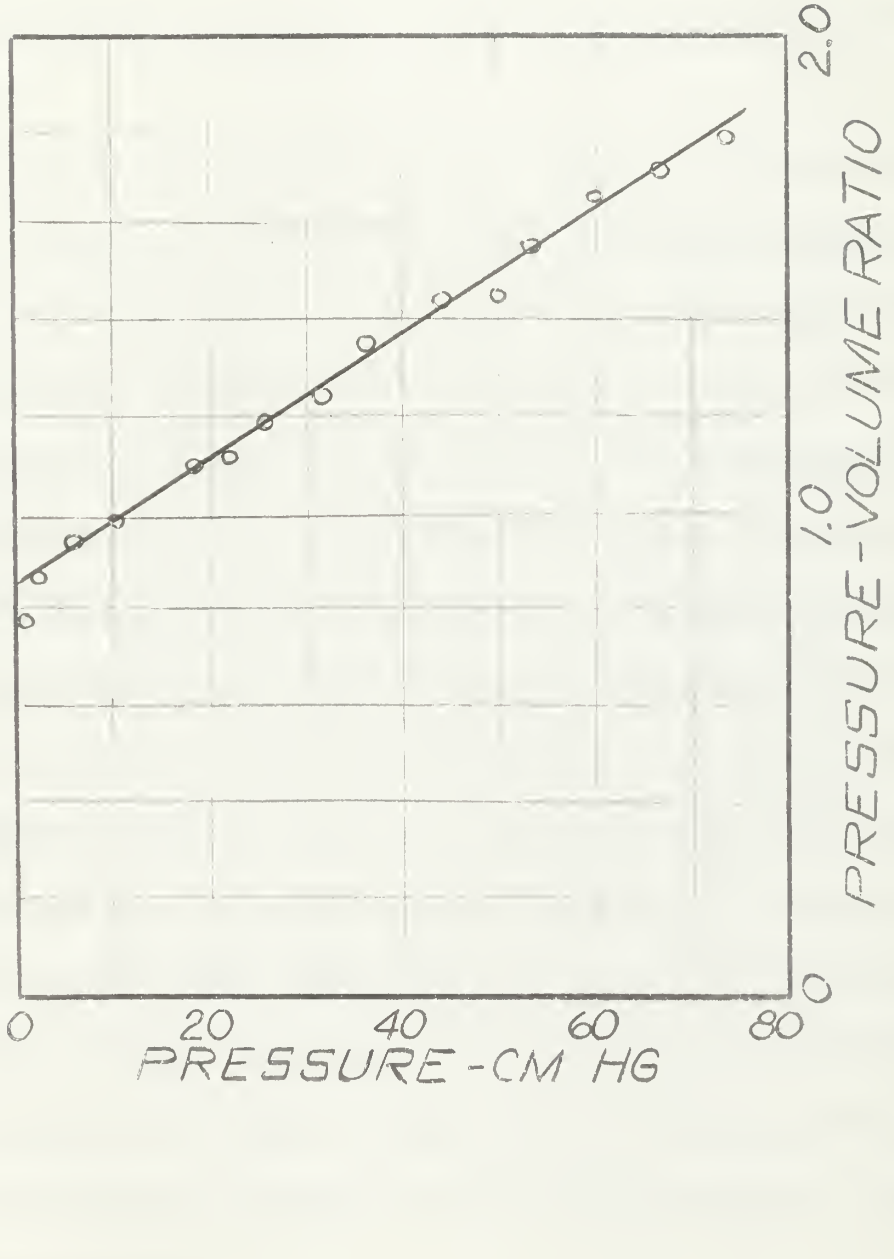


Figure 4. Langmuir Isotherm Plot



equation for this grade of charcoal and carbon dioxide. Evaluation of slope and intercept data led to values of 0.01325 and 87.8 for k and v_u, respectively. Comparison of equations (1) and (5) leads to the conclusion that the k of equation (1) should equal the quantity $1/kv_u$ of equation (5). The respective values are k= 0.833 and $1/kv_u = 0.860$, a reasonable agreement considering the measurement and plotting errors involved.

In retrospection of the procedure and results for this phase of the project the following comments are tendered the reader who might desire to work with similar apparatus. The relatively large dead volume of the apparatus reduced the precision of the results quite markedly. It behooves the experimenter to make this volume a minimum by using capillary tubing in the manifold (See Figure 1) and reducing the length of the entire apparatus to the smallest feasible. If a gas burette of capacity twice as great as the dead volume of the apparatus (at atmospheric pressure) is used, it will be unnecessary to refill the burette during a run. A sensitive vacuum gage (alphatron type or similar) would increase pressure measurement precision, especially in the very low pressure region. It is recommended that a vertical capillary tube, open ended, be inserted in the apparatus with its base joined to the gas burette at or near the point where the flexible tubing of the leveling bulb is joined. Volume readings could then be made precisely, after leveling the mercury in the capillary and burette, with the aid of a cathetometer.

6. Adsorption Chromatography - General.

The term "chromatography" as presently used encompasses a number of somewhat diverse processes which, in general, involve a column containing a substance (known as the stationary phase) through which a sample of a mixture is caused to be transported. This movement is effected by a fluid known as the mobile phase. The stationary phase may be either a solid adsorbent or a liquid and the mobile phase may be either a gas or a liquid. The stationary phase selectively retards the components of the mixture causing them to be moved through the column at differing rates; thus effecting a separation. The detection, characterization, and isolation of the segregated components at the column exit is the object of the chromatographic process. It is seen that the distribution of the components of the sample over two phases is the basis of chromatography. In adsorption chromatography the sample is caused to be distributed between the solid adsorbent and the moving fluid phase and separation of components results mechanically from the fact that the moving phase moves along the adsorbant.

Adsorption chromatography may be carried out by three different techniques. In elution development a small sample of the gas mixture is charged into the top of a column of solid adsorbent and a slow current of an inert (or very slightly adsorbed) gas is introduced which washes the sample through the column. The components of the sample, originally overlapping, travel down the column at speeds relative to their strength of adsorption. If these strengths differ sufficiently, the components segregate into "bands"

of component in inert gas solution separated by zones of pure eleunt. As the bands elute from the column they may be detected by a sensing device. Elution adsorption chromatography generally yields rather asymmetric peaks with steep fronts and long diffuse tails, resulting in somewhat poor separations. This is discussed in detail below. On the other hand, it should be noted that for components of very low boiling point, the asymmetry of the peaks is far less marked and it has proved possible to separate components such as hydrogen, nitrogen, oxygen, methane and carbon monoxide. Elution adsorption chromatography has been used to advantage for these light gases. In the case of gas-liquid partition chromatography elution peaks are generally symmetric.

In the frontal analysis technique of adsorption chromatography, the sample mixture is continuously introduced into the stream of inert gas in constant proportion. The components of the mixture will each saturate the adsorbent successively in order of increasing adsorptivity. As a component adsorbate is saturated additional sample will cause that component to "break through" the column exit, there to be detected by the sensing device. The components will thus elute successively depending on their adsorptivities, but with the exception of the first one, in impure form.

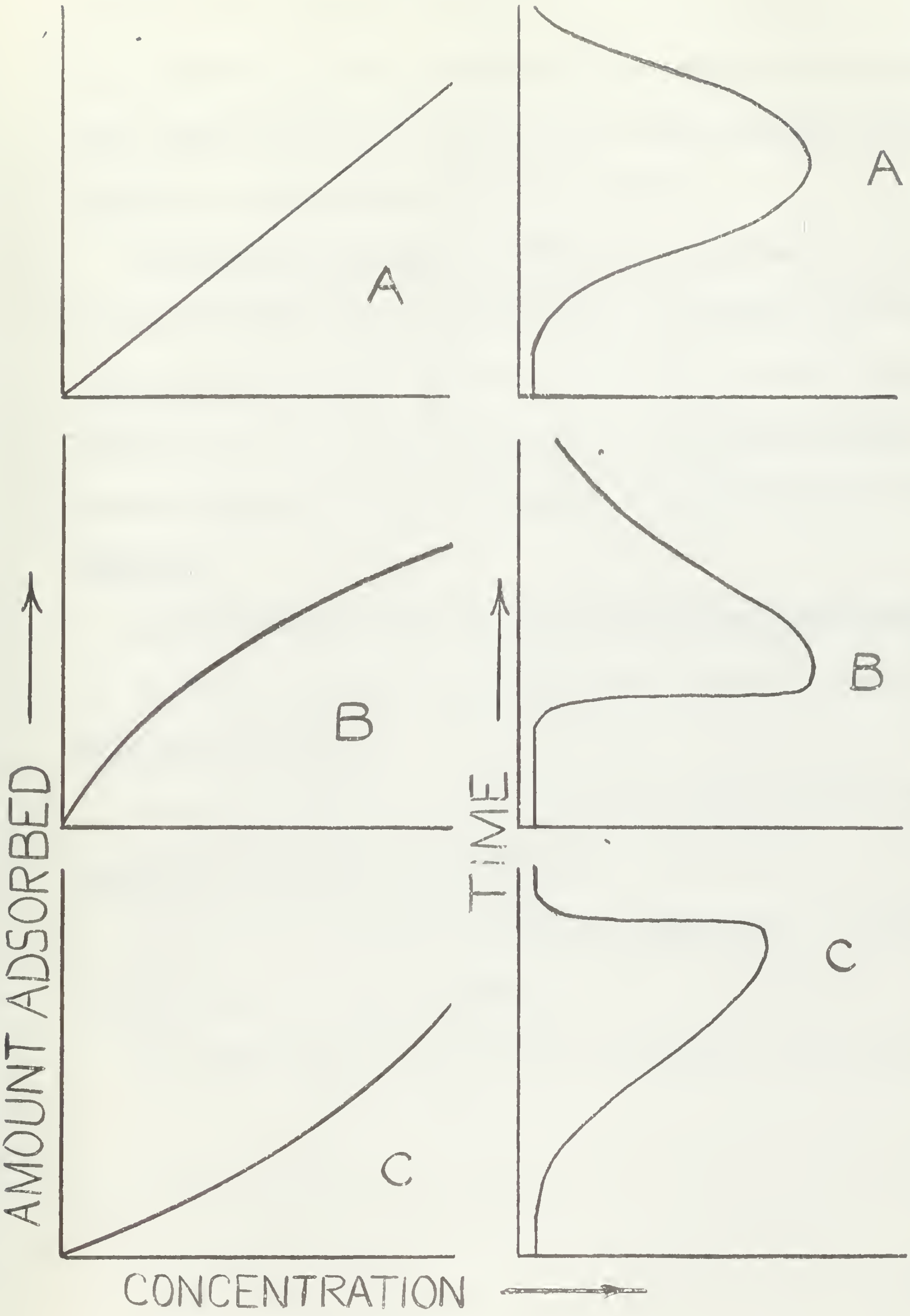
The displacement development technique consists of charging a column with a sample and subsequently admitting a stream of a very powerfully adsorbed gas. The latter displaces the components of the sample mixture forcing them down the column and out in order of increasing adsorptivity.

7. Chromatographs.

The eluent-gas concentration versus time trace (chromatograph) resulting from an elution analysis, for a single component sample, will approximate one of the three types shown in Figure 5. Type A, the symmetrical Gaussian distribution, indicates a linear isotherm. Types B and C, respectively, indicate isotherms curving toward the pressure axis (Langmuir type) and away from the pressure axis. Type A chromatograph is produced by most partition columns for moderate sample sizes. It is of interest here only insofar as the theory of linear adsorption chromatography has been developed rather extensively and an analogous theory for Langmuir adsorption will be developed below. As the sample size is increased a marked sharpening of the rear boundary of the chromatograph is noted indicating curvature of the isotherm away from the pressure axis at high concentrations (Type C). Type B (Langmuir adsorption) is of primary interest in this paper. An actual example of this type is shown in Figure 16. It is generally the result of adsorption on charcoal or silica gel. An exception to be noted is cited by Phillips (Ref. 12) for the adsorption of water vapor on charcoal at 20°C which behaves as Type C. Another observation of interest is that in Type A an accurate value of the distribution coefficient of the substance between stationary and mobile phases can be obtained by measuring the volume of inert mobile phase passed before the peak appears (Ref. 10).

A substance having Type A behavior produces a single sharp step when the substance breaks through the column if the frontal analysis technique

Figure 5. Typical Elution Chromatographs and Related Isotherms



is used. From the time before breakthrough and the concentration of sample in the entering mobile phase stream one can calculate the amount of substance retained on the column. This technique was utilized by James and Phillips (Ref. 7) in determining linear adsorption isotherms for benzene and cyclohexane on charcoal at 70°C.

In displacement analysis, a component is adsorbed on a fraction of the column proportional to its step length and inversely proportional to the breakthrough time of the displacer. The equilibrium vapor concentration is the same as that at which the step for that component is formed. Thus adsorption isotherms for linear adsorbates can be determined by this technique also.

James and Phillips (Ref. 7) report the following other pertinent items:

a. The sensitivity of the sensing device (thermal conductivity cell) is relatively unimportant.

b. In displacement analysis and in frontal analysis only linear adsorption isotherms can be determined.

c. No information can be obtained on hysteresis, i.e. only the ascending isotherm can be determined.

d. Irreversible adsorption can not be studied in this fashion.

8. Adsorption Chromatography Theory.

The theory of adsorption chromatography has had extensive treatment in the literature since its first formulation by Wilson (Ref. 15). However, almost no work has been reported on non-linear adsorption chromatography.

The following assumptions are made:

a. Diffusion along the column can be neglected.

b. The column is of uniform cross-section.

c. The column is uniformly packed with a homogeneous adsorbant.

d. The mobile phase flows at a constant linear velocity through the column.

e. The adsorbate distributes itself in accordance with the Langmuir equation between mobile phase and adsorbant.

f. Equilibrium between adsorbant and adsorbate exists at all times.

The assumption of negligible diffusion is open to question. The rate of diffusion, being proportional to concentration gradient, may be appreciable, especially at the front of a band. However, this simplifying assumption must be made originally, although it may be corrected for subsequently.

Though an over all equilibrium between adsorbant and adsorbate will not be present in the usual chromatographic analysis, owing to the differential nature of the process, equilibrium will be assumed.

This approach to the analysis of non-linear adsorption elution chromatography is an extension of a theoretical analysis described by Keulemans

(Ref. 9) for linear partition chromatography.

Consider three successive adsorption vessels as in Figure 6 out of a series of j vessels, numbered 1, 2, 3, . . . j. Let the ordinal numbers of these vessels be designated r−1, r, and r + 1. A finite amount of adsorbate is introduced into the first vessel where a fraction of it is adsorbed on the adsorbant. A steady flow of carrier gas (non-adsorbed) passes successively through the vessel carrying with it the unadsorbed adsorbate. It is assumed that at any time the volume of inert gas, V_G, is the same in all vessels and that the amount of adsorbant, M_S, is the same for all vessels. Also assume a steady flow of carrier gas and that at any time each vessel is in equilibrium.

We now define $X_{S,r}$ as the concentration of the adsorbate in the adsorbant in vessel r, and $X_{G,r}$ as the concentration of adsorbate in the gas phase in vessel r. $X_{S,r}$ has dimensions of milliliters per milliliter of carrier gas. Then if p_r is the partial pressure of the adsorbate in vessel r:

$$p_r = \left[\frac{X_{G,r} V_G}{V_G + X_{G,r} V_G} \right] P_r^o \qquad (6)$$

$$= \left[\frac{X_{G,r}}{1 + X_{G,r}} \right] P_r^o \qquad (7)$$

where P_r^o is the total pressure of carrier gas plus adsorbate in vessel r.

If it is assumed that equilibrium is established in each vessel according to the Langmuir equation, equation (5), we can rewrite the Langmuir isotherm, in terms of the quantities defined above for vessel r, thus:

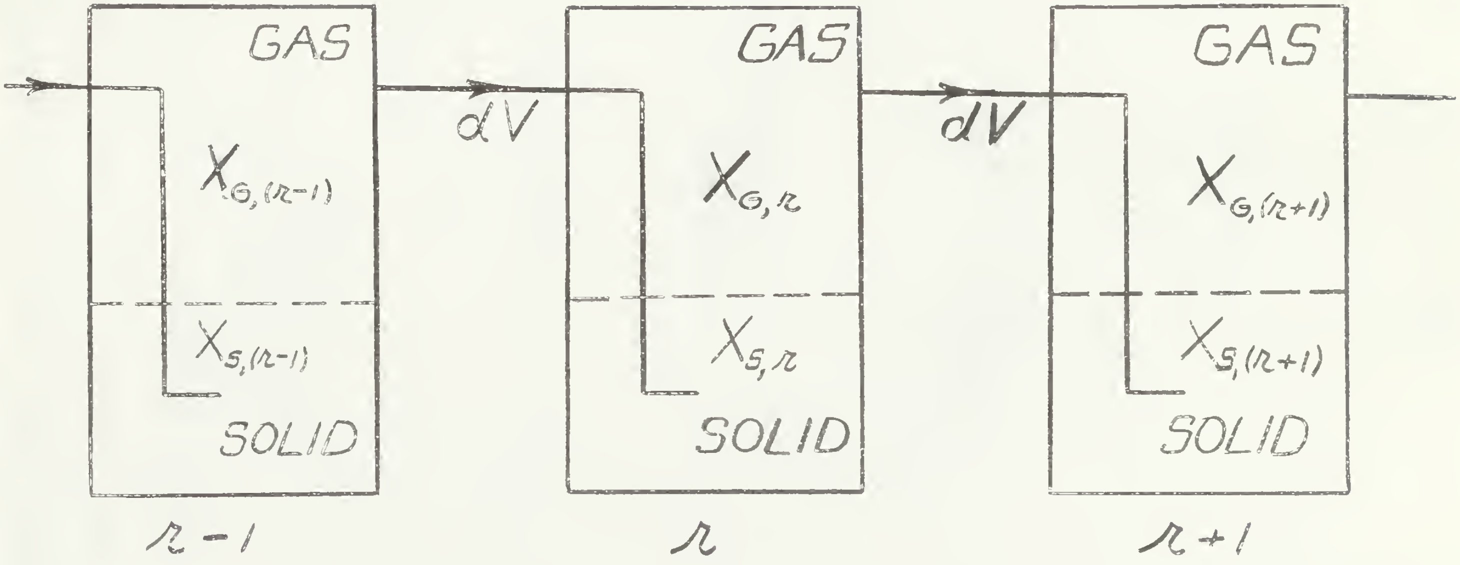


Figure 6. Three Successive Adsorption Vessels

$$\frac{p_r}{X_{S,r}} = \frac{1}{v_u k} + \frac{p_r}{v_u} \tag{8}$$

Solving for $X_{S,r}$:

$$X_{S,r} = \frac{v_u k\, p_r}{1 + k\, p_r} \tag{9}$$

Substituting equation (7) for p_r and simplifying:

$$X_{S,r} = \frac{v_u k P_r^{\circ} X_{G,r}}{1 + \left[1 + k P_r^{\circ}\right] X_{G,r}} \tag{10}$$

Combining constants:

$$X_{S,r} = \frac{X_{G,r}}{a + b X_{G,r}} \tag{11}$$

where:

$$a = 1/P_r^{\circ} v_u k \tag{11a}$$

and

$$b = a + 1/v_u \tag{11b}$$

Differentiating equation (11):

$$dX_{S,r} = \frac{a\, dX_{G,r}}{\left(a + b X_{G,r}\right)^2} \tag{12}$$

If a differential volume, dV, of carrier gas enters vessel r from vessel r-1, it will carry with it an amount $X_{G,(r-1)}\,dV$ of adsorbate. Simultaneously, an equal differential volume leaves vessel r carrying with it $X_{G,r}dV$ of adsorbate into vessel r+1. Note that $X_{G,r} \neq X_{G,(r-1)}$. Therefore, the total adsorbate content of vessel r has changed. The concentra-

tion of the adsorbed phase has changed by $dX_{S,r}$ and that in the mobile phase by $dX_{G,r}$; or, the amount of adsorbate in vessel r has changed by $M_S dX_{S,r}$ in the adsorbed phase and $V_G dX_{G,r}$ in the mobile phase. A material balance about vessel r yields:

$$X_{G,(r-1)}dV - X_{G,r}dV = V_G dX_{G,r} + M_S dX_{S,r} \tag{13}$$

Combining equations (12) and (13), $X_{S,r}$ can be eliminated:

$$\frac{dX_{G,r}}{dV} = \frac{X_{G,(r-1)} - X_{G,r}}{V_G + M_S\left[\frac{a}{(a+bX_{G,r})^2}\right]} \tag{14}$$

This equation can be evaluated for the first vessel (r=1) by the method of partial fractions (Ref. 6). The solution is:

$$\frac{M_S}{a}\ln_e\frac{a+bX_{G,1}}{X_{G,1}} - V_G\ln_e X_{G,1} - \frac{M_S}{a+bX_{G,1}} = V \tag{15}$$

Unfortunately, equation (15) cannot be solved explicitly for $X_{G,1}$, thus preventing a general solution to equation (14) by the procedure of iteration and induction. However, the following deductions can be made from equation (15).

The general solution of equation (14) will probably be of an exponential form. Assuming the following

$$X_{G,r} = A\exp(\alpha' V + \beta') + B' \tag{16}$$

to be a general solution, it can be said that A is a function of column length and sample size, α' and β' are parameters dependent on the adsorbant-adsorbate pair and sample size, and B' is a function of the ordinal number of the vessel (r).

Consider now a chromatographic adsorption column made up of a large number of theoretical vessels of the type postulated above. At any time after the column is charged, the distribution of adsorbate in the gas phase in adjacent sections of the column will be as predicted by equation (16). In other words, this equation should predict the gas phase concentration profile over the length of the column at any time. By varying the time and looking only at the j'th vessel, the column exit, one can see the entire concentration profile passing progressively out the exit of the column. For a constant flow rate of the mobile phase, equation (16) can then be rewritten as a function of time, thus:

$$X_{G,j} = A \exp \alpha(t+\beta) + B \tag{17}$$

where α and β are new parameters, B is a function of column length and A remains as defined. The analytical determination of A, B, α, and β, is dependent on the solution of equation (14). The evaluation of these unknowns empirically from experimental results is described below. The results will be of only academic interest and the problem of determining the constants of the Langmuir equation remains.

9 Chromatographic Apparatus.

The apparatus used for obtaining the elution chromatographs was a Model 154-C Vapor Fractometer manufactured by the Perkin-Elmer Corporation, Norwalk, Conn. A flow schematic of the instrument is shown in Figure 7.

The carrier gas, which conveys the sample through the apparatus, was chosen to be helium because of its high thermal conductivity, relatively low cost, high purity, and availability. The rate of flow of the carrier gas was adjusted with the pressure regulator in order to get relatively broad bands on the chromatograph, for the various sample sizes in a reasonable time. The broad bands were desirable in this case (though not normally when separation is desired) in order to increase the measurement precision of subsequent numerical analysis. The samples were introduced into the apparatus at ambient temperature by means of a precision gas sampling valve which provided for the charging of reproducible sample volumes. Four precision sample volume tubes were available in sizes 1/4cc, 1cc, 5cc, and 25cc. The column and detector were enclosed in a thermostatically controlled chamber permitting temperature control to better than one degree centigrade. The detector consisted of a dual thermal conductivity cell through the reference side of which the carrier gas was diffused prior to sample injection. Column eluent passed through the sensing side of the detector. A thermistor circuit measured the thermal conductivities of the atmospheres in the detector chambers and via a bridge circuit any difference in conductivities of the two sides was

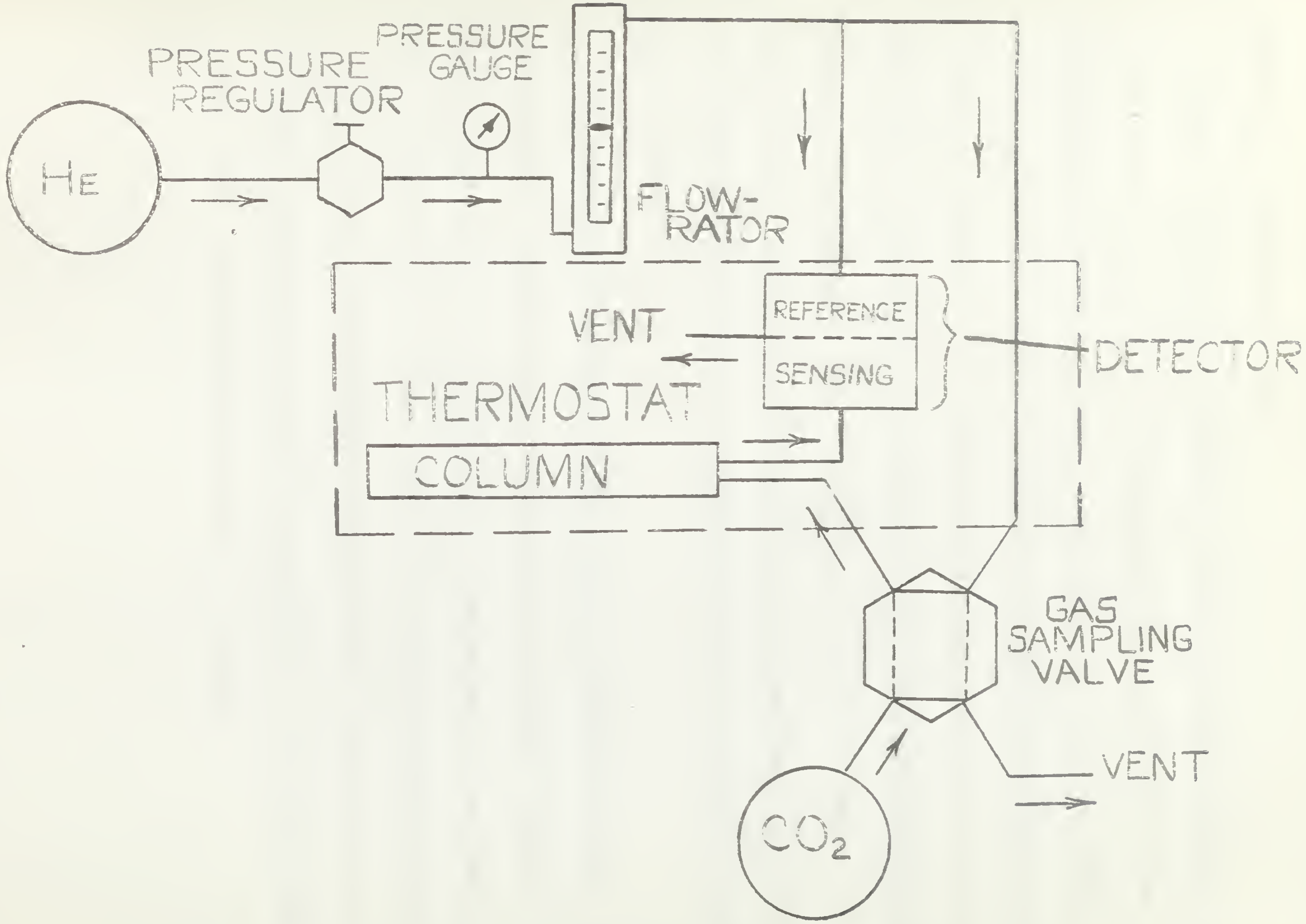


Figure 7. Flow Schematic of Vapor Fractometer

caused to be displayed on a Speedomax Type G (Leeds and Northrup Co.) Recorder. A recorder range control permitted attenuation of detector signals over a range of one to 512.

Several columns were constructed of 6 mm Pyrex Glass tubing ranging in length from 100 to 180 cm. For the purposes of this project it was determined that the 180 cm column satisfied the requirements of being long enough to yield a reasonably diffuse chromatograph and short enough to complete a sample run in a relatively brief time for the various sample sizes used. The adsorbant used was high activity charcoal marketed by Burrell Corp., Pittsburgh, Pa., (Catalogue No. 341-10) of mesh size B.S.S. 30-80. The columns were prepared and outgassed in accordance with standard chromatograph practice (Refs. 8, 9) and dried prior to each run at 180°C.

The thermostat temperature was chosen to be 70°C for all runs. This temperature allowed good temperature control on the vapor fractometer and at the same time permitted the use of a water bath for temperature control in the adsorbtion apparatus. The column pressure drop for all runs was adjusted to 15.0 psi which gave a reproducible helium flow rate of 150 ml/min. Attenuation was used as necessary for the various sample sizes in order to keep the recorder trace on the chart.

10. Chromatograph Procedure

The column, after insertion in the fractometer, is baked out while maintaining a stream of fresh helium through the apparatus to flush out any impurities. The thermostat is then adjusted, the column pressure set, and the proper size sample tubing installed. After a constant temperature is obtained, the recorder and detector are turned on, the detector voltage is adjusted and the recorder base line is zeroed. Carbon dioxide is allowed to flow through the sample tubing with the gas sampling valve in the vent position. The stability of the base line gives an indication that the entire apparatus is at constant temperature. The run is started by turning the gas sampling valve to the sample-in position and a notation made on the recorder trace at this point. Readings are taken on column number, temperature, pressure, flowmeter, sample size, and attenuation. The sample gas supply may now be shut off. The recorder trace is watched to ensure the proper attenuation of the peak when it occurs. Time markings on the recorder trace are unnecessary since the recorder runs at constant speed (0.5 inches/minute). When the recorder trace returns to the base line (or very nearly so) after peaking, the run may be considered completed and the apparatus shut down.

11. Chromatographic Results

All quantitative results were obtained using the column described in Table I. In order to minimize the number of variable parameters involved, certain conditions were imposed on all runs. These are tabulated in Table II.

In all runs, the sample eluted with the expected chromatograph shape showing a sharp front and long diffuse tail, (See Figure 16). The smaller samples took an appreciably longer time to begin eluting and had relatively longer tails than the larger samples. The data on retention time (retention time is defined as $t_1 - t_o$), peak height, and area under peak are summarized in Figures 10, 11, and 12. The data in these figures has been plotted on logarithmic scales in order to conveniently span the ranges involved.

The elution chromatographs for the various sample sizes were analyzed numerically by the method of least squares described by Milne (Ref. 11). A representative calculation is shown in Appendix I. The general form of equation (17) was used and the value of B was taken as constant (equal to zero) since it depends only on the column length, which was the same for all runs. Mean results of these calculations are shown in Table III. The values of $X_{G\,r}$ for the tabulated values are in arbitrary units of displacement from recorder base line for time, t, taken in minutes from breakthrough time. The displacement of the recorder is caused by a change in thermal conductivity of the eluent gases, which is proportional to the carbon dioxide concentration. The results are relative and applicable only to the

FIGURE 8

TABLE I

COLUMN CHARACTERISTICS

Length	180 cm
Material	standard pyrex tubing
Size	6mm
Length of Packed Section	178cm
Packing	Burrell Corporation High Activity Charcoal Catalog #341-10
Packing Weight	9.50g
Packing Mesh Size	B.S.S. 30-80
Packing Density	5.34mg/cm of length

FIGURE 9

TABLE II

RUN CONDITIONS

Temperature of Column	70°C
Pressure Across Column	15 psig
Exhaust Pressure	ambient
Helium Flow Rate	150 ml/min
Detector Temperature	70°C
Sample Injection Pressure	ambient
Flowrator Reading	52mm

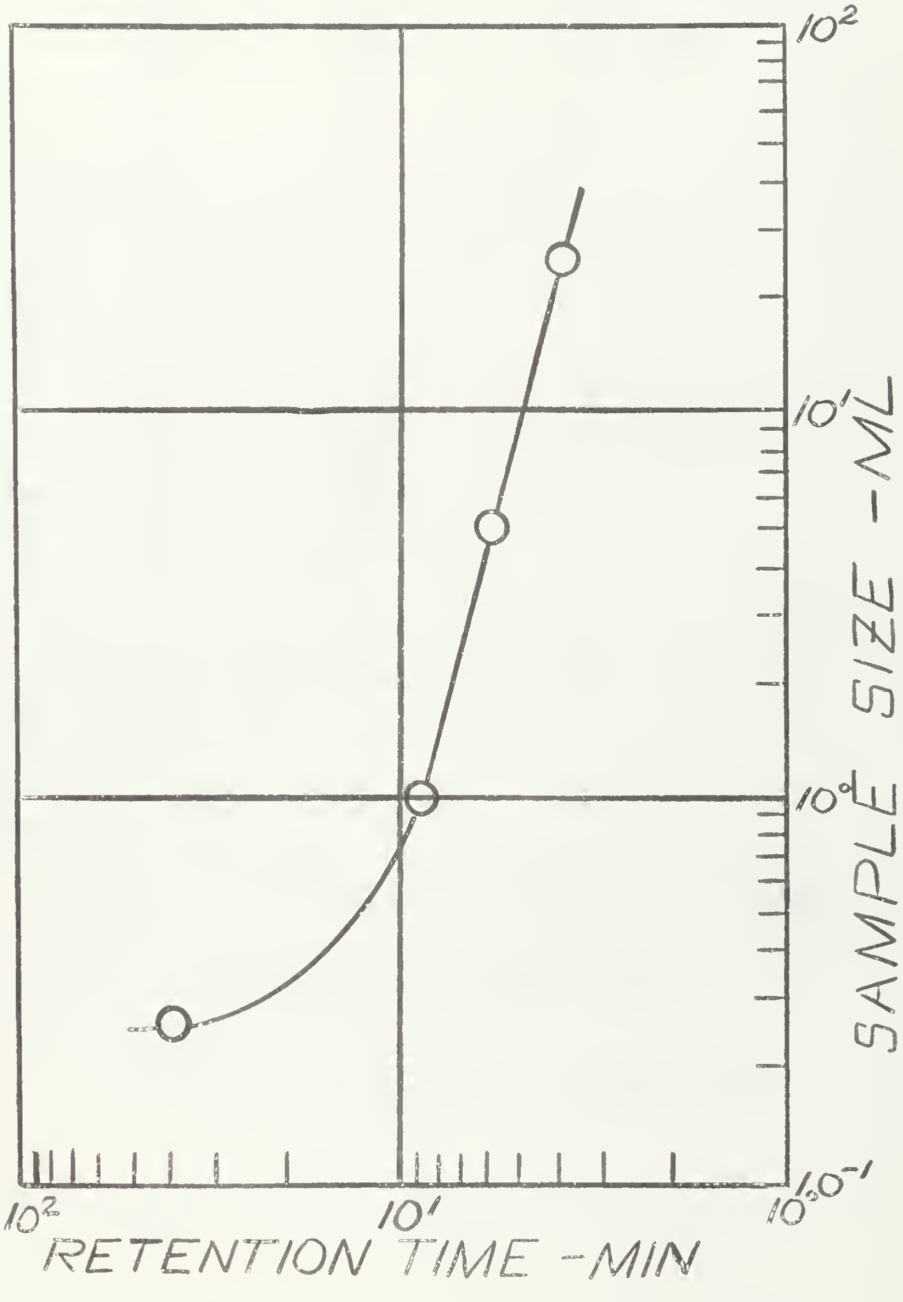


Figure 10. Retention Time vs. Sample Size

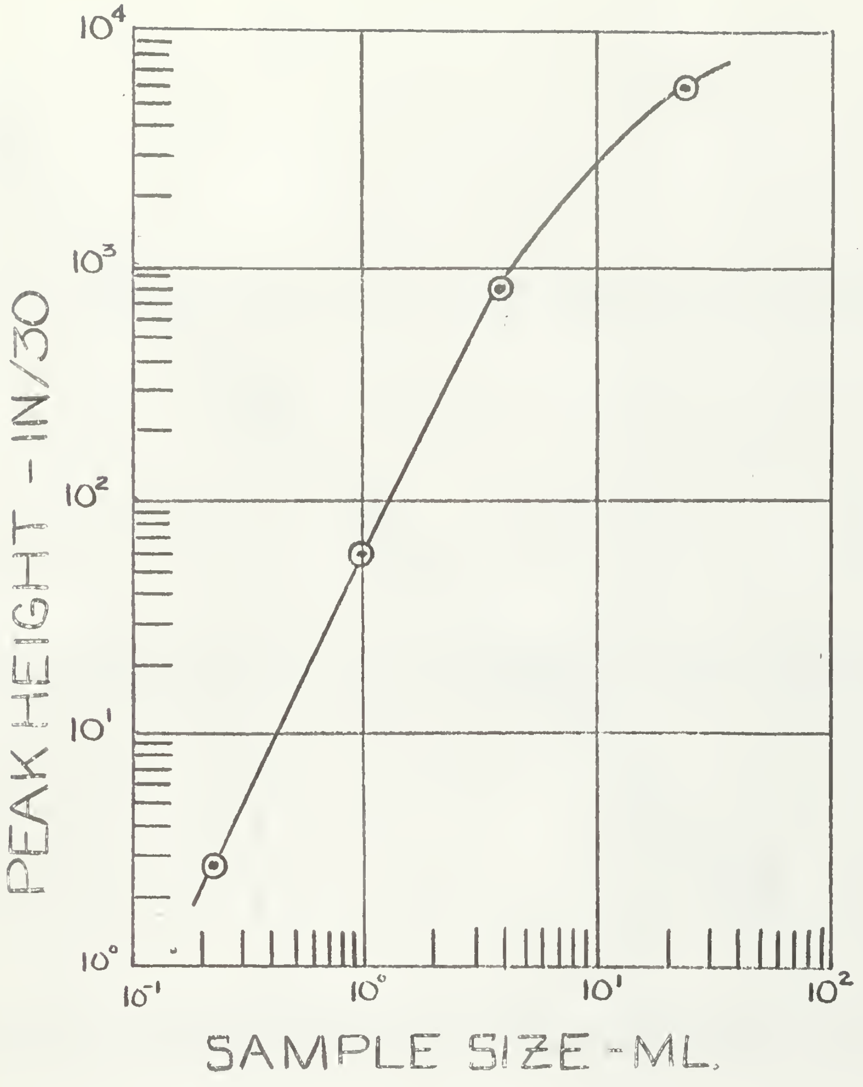


Figure 11   Peak Height vs. Sample Size

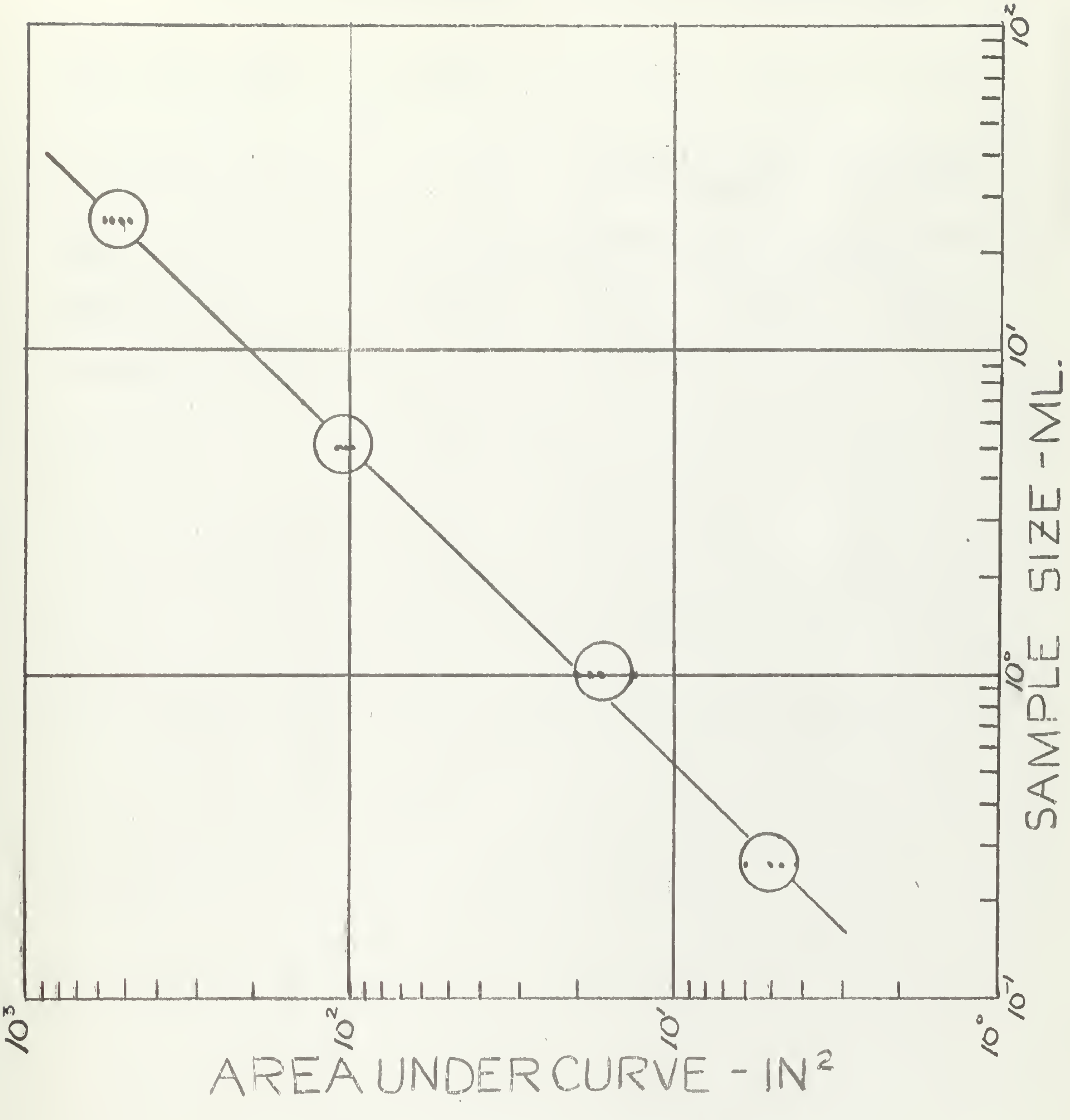


Figure 12 Area vs Sample Size

FIGURE 13

TABLE III

VALUES OF PARAMETERS BY METHOD OF LEAST SQUARES

Sample Size (ml)	0.25	1	5	25
A (arbitrary units)	596	2478	38,400	320,000
α (min^{-1})	-0.0431	-0.1273	-0.4150	-0.7175
β (min^{-1})	-0.40	-0.33	-0.25	-0.25
B (arbitrary units)	0	0	0	0

data of this project. Note that values of β were arbitrarily chosen for ease of calculation and do not affect the values of α or A. A plot of A versus sample size (Figure 14) indicates a linear relationship in the smaller sample size range. For larger samples the deviation from linearity may be attributed to column saturation, diffusion or other factors not considered. Values of α increase progressively with sample size, as expected and shown in Figure 15.

In conclusion, it may be said that the determination of adsorption parameters by purely analytic procedures using gas chromatography leads to some extremely complicated, cumbersome equations. However a semi-analytic technique may yield useful results. Further work along these lines is indicated, particularly with respect to the effect of variables other than sample size on the parameters of the elution curve.

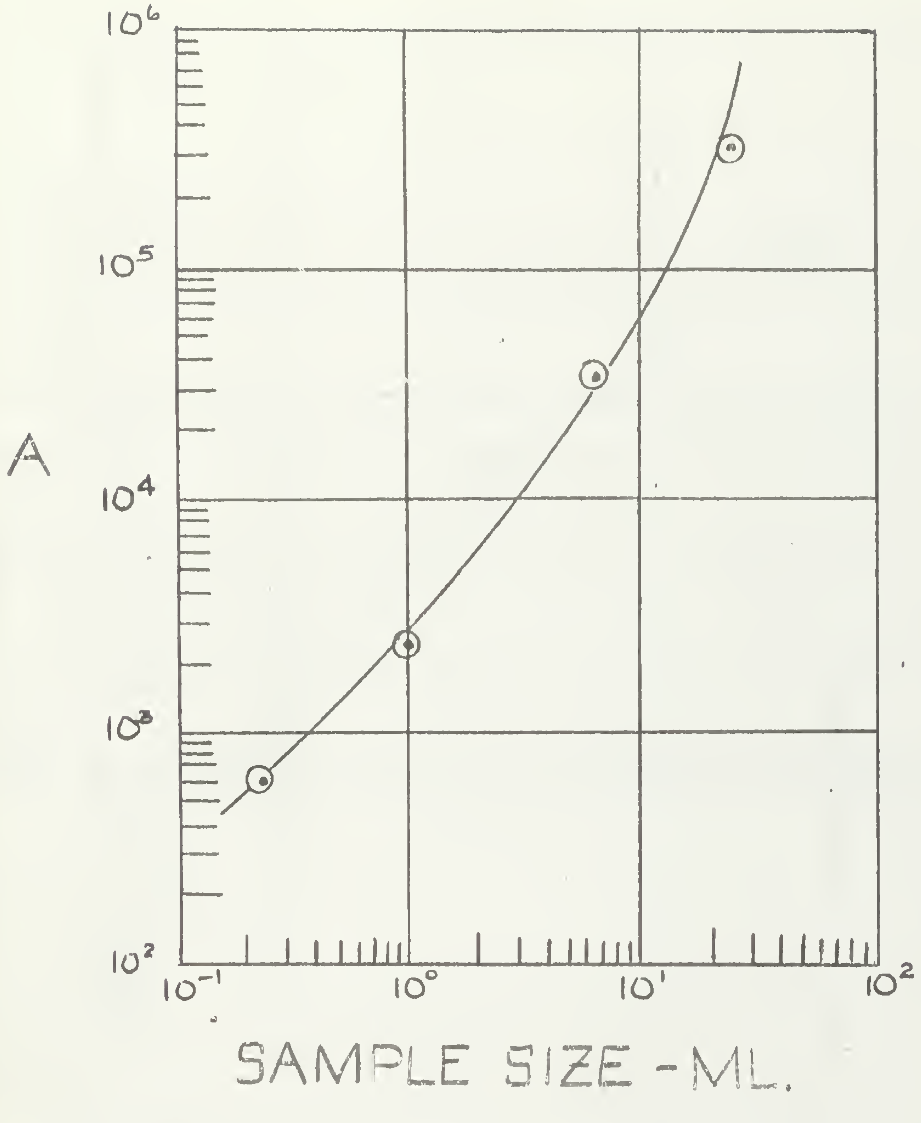


Figure 14. Parameter A vs. Sample Size

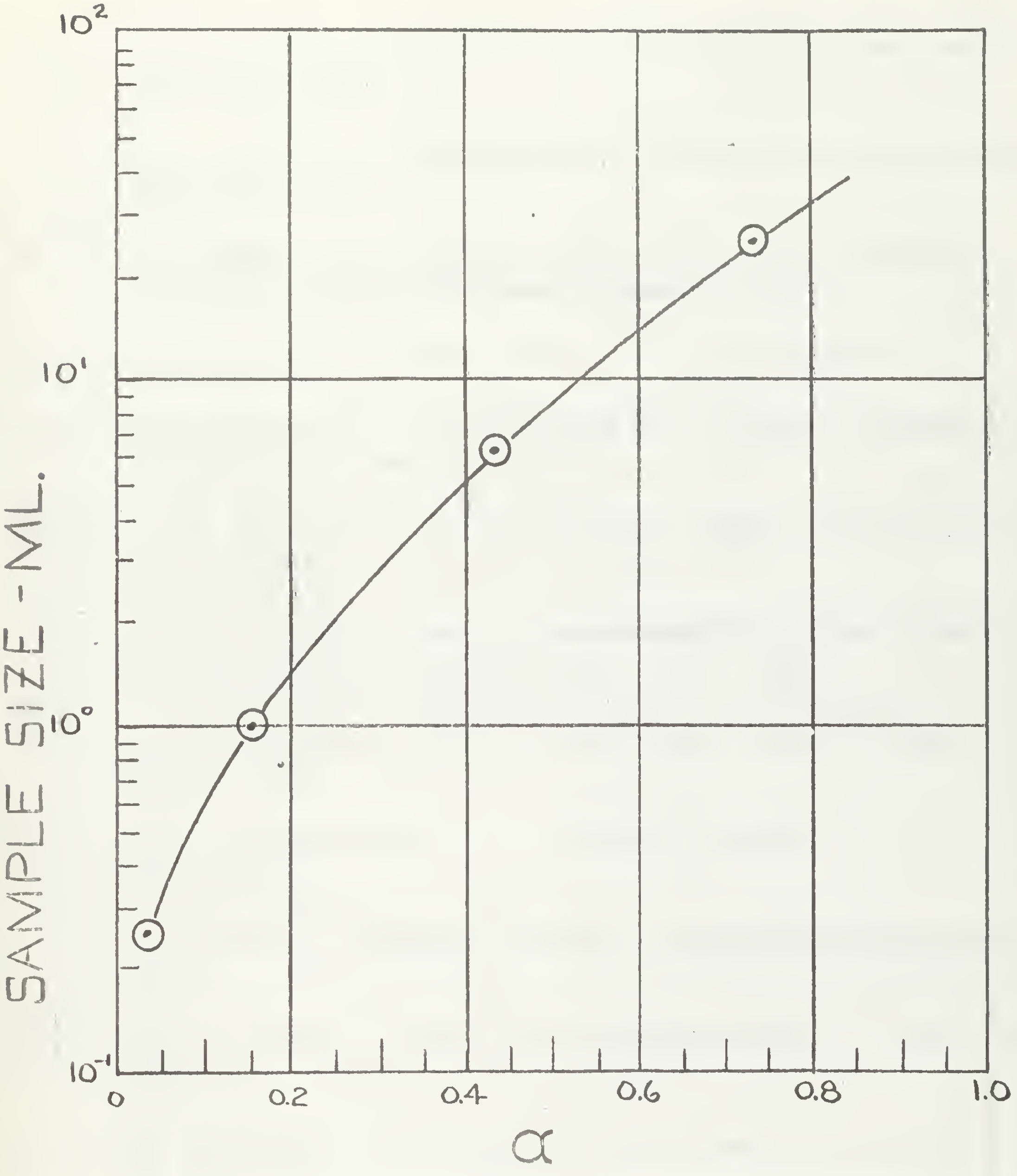


Figure 15. Sample Size vs. Parameter α

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APPENDIX I

EXAMPLE OF NUMERICAL ANALYSIS OF A CHROMATOGRAPH

The approximation of an elution curve by an exponential equation of the type $S = A \exp \alpha(t-\beta)$ is illustrated here using the method of least squares described by Milne (Ref. 11). This particular method was chosen in order to minimize the effect of random errors.

The calculation here described is for Run #43 in which a 1 ml sample was run through the apparatus under the same conditions described in the body of this report. Figure 16 illustrates the elution curve obtained. For convenience in calculations the β term of equation (17) is set at -0.33 min. Data are shown in columns 2 and 3 of Table IV. S is the displacement of the curve at time $t' = t - \beta - t_1$ in arbitrary units from the base line. The parameters

$$y = \ln_e S,$$

$$a_o = \ln_e A,$$

and

$$a_1 = \alpha$$

are then defined and the remaining columns of Table IV calculated, with each column summed underneath. This yields the following equations:

$$19\,a_o + 171\,a_1 = 113.32471$$

$$171\,a_o + 2109\,a_1 = 947.52222$$

These, when solved simultaneously, yield:

$$a_o = 7.12$$

$$-a_1 = 0.1273$$

Taking the antilog of a_o and multiplying by the attenuation, the result is

obtained:

$$S = 2478$$

$$-\alpha = 0.1273$$

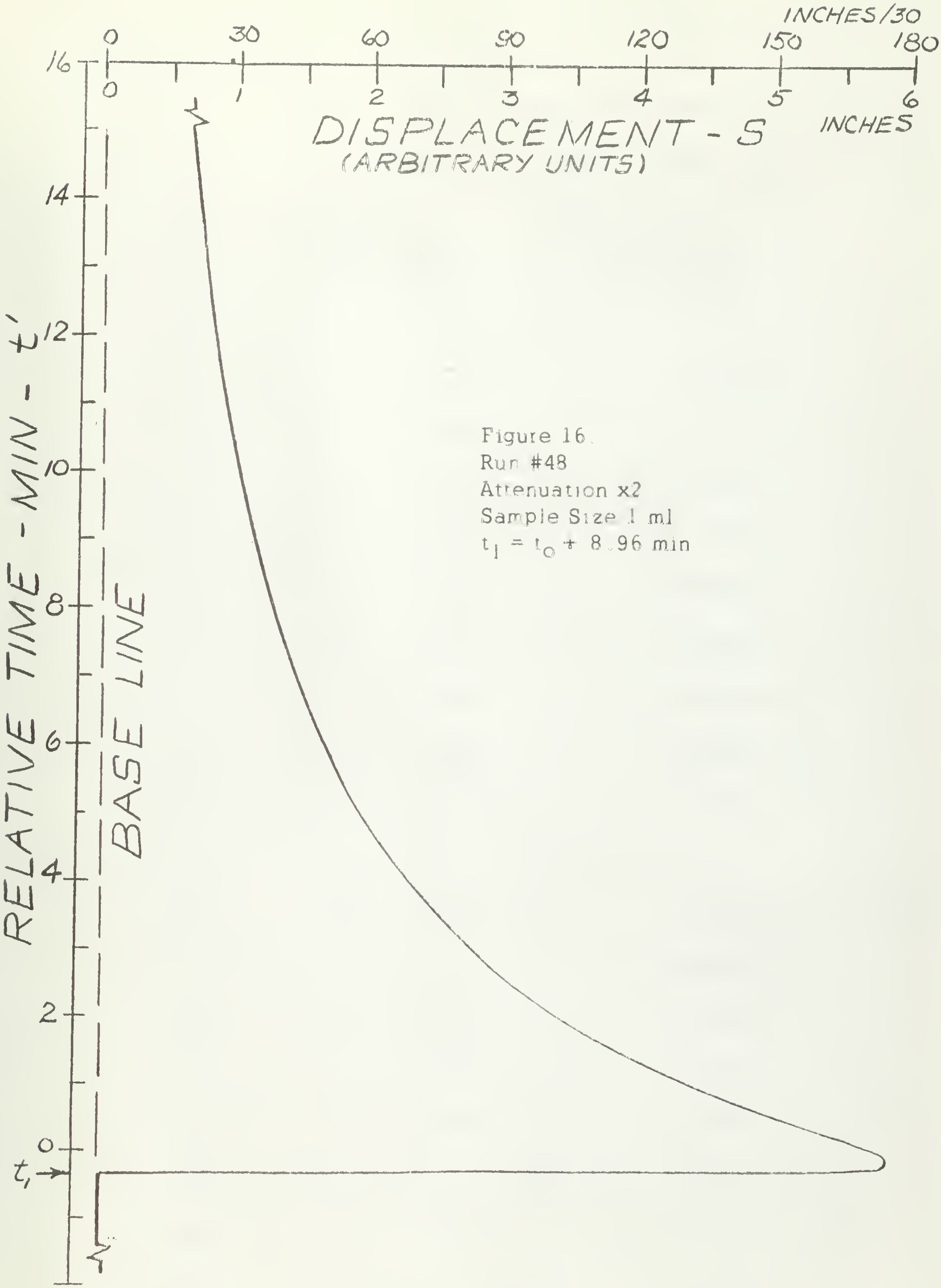

Figure 16.
Run #48
Attenuation x2
Sample Size 1 ml
$t_1 = t_0 + 8.96$ min

FIGURE 17 TABLE IV

SAMPLE CALCULATIONS FOR RUN #48

(1)	(2) t'	(3) S	(4) y	(5) $(t')^2$	(6) yt'
1	0	1745	7.46451	0	6
1	1	1335	7.19668	1	7.19668
1	2	1030	6.93732	4	13.87464
1	3	820	6.70930	9	20.12790
1	4	675	6.51471	16	26.05884
1	5	570	6.34564	25	31.72820
1	6	495	6.20456	36	37.22736
1	7	425	6.05209	49	42.36463
1	8	375	5.92693	64	47.41544
1	9	335	5.81413	81	52.32717
1	10	305	5.72031	100	57.20310
1	11	275	5.61677	121	61.78447
1	12	250	5.52146	144	66.25752
1	13	225	5.41610	169	70.40930
1	14	205	5.32301	196	74.52214
1	15	190	5.24702	225	78.80530
1	16	175	5.16479	256	82.63664
1	17	165	5.10595	289	86.80115
1	18	155	5.04343	324	90.78174
19	171		113.32471	2109	947.52222

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